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The Use of the Rotating Anode in Electrolytic Separations

THESIS

Presented to the Faculty of the Department of Philosophy
of the
University of Pennsylvania
in Partial Fulfilment of the Requirements
for the Degree of
Doctor of Philosophy,

BY

MARY ELISABETH HOLMES

MYSTIC, CONN.

1908

HODGES & KIRK
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INTRODUCTION.

This investigation was undertaken for the purpose of proving whether satisfactory separations of metals could be made with the rotating anode, using low currents. Many separations with stationary electrodes have been made with low currents, but with the rotating anode, high currents of from three to five amperes have been employed. The largest contribution to the subject of metal separations, using the rotating anode, was made by Ashbrook in 1904 (*Journal of the American Chemical Society*, 26, 1285). All his work was done with high currents, five amperes being generally used. A few separations were later recorded by Miss Langness (Thesis, 1906), in which low currents and rotation were successful. Silver was separated from copper, nickel, platinum or zinc, using the cyanide electrolyte, the current ranging from 0.25 to 0.4 amperes. The analysis of a coin, as performed by Miss Langness, was made possible by the fact that silver could be deposited completely by such a low current as 0.4 ampere, while the copper required a much higher current. The time given to these silver separations was about twenty minutes. These results would seem to indicate the possibility of obtaining other separations with low currents in comparatively short periods of time.

Criticism of the rapid methods of electrolytic work has often been made to the effect that while the methods employed may be adequate for the determination of single metals, the introduction of more than one metal into the solution causes such a variation in conditions that separations are not practicable. The only answer to such doubts is a systematic study of the whole subject of separations, varying conditions of current, rotation, time and electrolyte used, so that for each metal all possibilities may be determined. Through the following work, a beginning of such study has been made with the element cadmium. The possibilities of its separation at low currents from the metals of Groups III and IV, and from magnesium, have

been ascertained, and a comparison made of these results with those previously obtained with high currents.

The conditions of work were as follows. The current was kept in almost all cases below one ampere. Currents below 0.3 or 0.4 ampere were not found useful. The rotating dish anode used first by Miss Langness (Thesis, 1906) was employed. The cathode was a platinum dish of 200 c. c. capacity, the usual form of dish used in electro-analysis. The time required for a determination was about forty-five minutes, or one hour, and the electrolytes used were (1) sulphuric acid, and (2) ammonium acetate and acetic acid.

EXPERIMENTAL PART.

A. SULPHURIC ACID ELECTROLYTE.

I. Precipitation of cadmium alone. A solution of cadmium sulphate was used, containing about 0.2 g. of cadmium metal in 10 c. c. The first problem was the determination of the lowest possible current at which the cadmium could be completely precipitated. Varying quantities of sulphuric acid were tried, the best results being obtained with 1 c. c. or 0.5 c. c. of acid of specific gravity 1.09. The solution was not heated before electrolysis. Ten c. c. of cadmium sulphate were placed in the platinum dish, the desired amount of sulphuric acid added, the solution diluted to 60 c. c., and then electrolyzed at room temperature. The volume of solution should not exceed 60-65 c. c. when the dish anode is used, in order that splashing may be avoided. A speed of 300-400 revolutions a minute gave the best results. The deposits were smooth and adherent, with fine crystals in the center of the dish. It was found that washing with hot water tended to loosen these crystals, and loss was thereby incurred. Cold water was therefore used for washing, except in special cases.

Results of this work were as follows:

	CdSO ₄ Cd in grams	H ₂ SO ₄ sp. gr. 1.09 c. c.	N. D. ₁₀₀ Amperes	Volts	Time	Cd found	Error in grams
1.	0.2070	1	0.1	2.5	4 hr. 10 min.	0.1959	-0.0111
2.	0.2070	1	0.2	2.75	45 min.	0.1625	-0.0445
3.	0.2070	1	0.3	2.75	1 hr. 20 min.	0.2068	-0.0002
4.	0.2070	1	0.3	2.75-3	1 hr. 15 min.	0.2067	-0.0003
5.	0.2070	1	0.3	2.75	45 min.	0.2063	-0.0007
6.	0.2070	1	0.3	2.75	45 min.	0.2069	-0.0001
7.	0.2070	1	0.3-0.4	3	45 min.	0.2074	+0.0004

It was therefore concluded that with a current of 0.3 ampere, complete precipitation of the cadmium could be obtained in forty-five minutes. An effort to decrease the time did not appear successful. In many of the following separations, the current was held at 0.4 ampere, sometimes raising it to 0.5 for the last ten or fifteen minutes.

II. Separation of cadmium from metals of Group III.

(a.) From aluminium.

Ten c. c. of cadmium sulphate solution and 25 c. c. of aluminium sulphate solution (0.1811 g. aluminium in 25 c. c.) were placed in the platinum dish, 1 c. c. sulphuric acid (sp. gr. 1.09) added, and the electrolysis conducted at room temperature.

	CdSO ₄ Cd in grams	Al ₂ (SO ₄) ₃ Al in grams	H ₂ SO ₄ sp. gr. 1.09 c.c.	N. D. ₁₀₀ Amperes	Volts	Time	Error in Cd found grams
1.	0.2051	0.1811	1	0.4	3	45 min.	0.2052 +0.0001
2.	0.2051	0.1811	1	0.4	2.75	45 min.	0.2051 0.0000
3.	0.2051	0.1811	1	0.4	2.75	45 min.	0.2054 +0.0003
4.	0.2051	0.1811	1	0.4-0.5	2.75	45 min.	0.2047 -0.0004
5.	0.2051	0.1811	1	0.4-0.5	2.75	45 min.	0.2047 -0.0004
6.	0.2051	0.1811	1	0.4-0.5	2.75	45 min.	0.2051 0.0000

Similar results were obtained by Ashbrook, using high currents.

(b.) From chromium.

The experiments with chromium were not so conclusive. The amount of cadmium deposited at 0.4 ampere was uncertain, generally low in weight. With a current of 0.7 ampere, the deposits were too high in weight, but after treating them with hot water, the weight became less, in some cases reaching the theoretical amount. The deposits were somewhat dark and irregular in appearance. They evidently occluded mother liquor, for on treating one deposit with nitric acid, and evaporating the solution to dryness, a greenish residue was obtained. No decisive test for cadmium was obtained from the filtrates of experiments 4 and 5. It is, therefore, probable that there is really a separation here, but not entirely clear-cut.

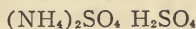
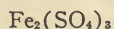
CdSO ₄		Cr ₂ (SO ₄) ₃		H ₂ SO ₄ N. D. ₁₀₀							
Cd		Cr		sp. gr. 1.09						Error in	
in grams		in grams		c.c.	Amperes	Volts	Time	Cd found	grams		
1. 0.2051	0.2635	0.5	0.4	2.8			1 hr.	0.2052	+0.0001		
2. 0.2051	0.2635	0.5	0.4	2.5			45 min.	0.1081	-0.0970		
3. 0.2051	0.2635	0.5	0.4-0.5	2.5-3			1 hr.	0.1696	-0.0355		
4. 0.2051	0.2635	0.5	0.4-0.75	3-4			1 hr.	0.2065			
			after washing with hot water					0.2053	+0.0002		
5. 0.2051	0.2635	0.5	0.4-0.55	2.75-3			1 hr.	0.2065			
			after washing with hot water					0.2057	+0.0006		
6. 0.1936	0.2763	0.5	0.7	3			1 hr.	0.1955			
			after washing with hot water					0.1952	+0.0016		

Ashbrook attempted to separate cadmium from chromium, using high currents, but states that in sulphuric acid solution, the deposit always weighed low. With phosphoric acid, however, he obtained a successful separation.

(c.) From iron.

1. Ferric iron.

A solution of ferric ammonium sulphate was used, containing 0.2554 g. of iron in 25 c. c. On electrolyzing 25 c. c. of this solution at 0.4 ampere and 1.75 volts for forty-five minutes, no deposit was obtained. From a mixture of 10 c. c. of the solution of cadmium sulphate with ferric ammonium sulphate (25 c. c.), only a slight deposit of cadmium was obtained at 0.4 ampere. A current of 0.8 ampere was then tried with the iron solution, and no deposit obtained. Electrolyzing a mixture of the cadmium and iron solutions with a current of 0.8-0.9 ampere, deposits of cadmium were obtained, but they were not of theoretical weight. In one case (exp. 2, given below), a little dilute sodium hydroxide solution was added during the electrolysis. The filtrate from this experiment showed no test for cadmium, but the deposit was contaminated with iron. In experiments 3 and 4, not only was iron found in the deposit, but cadmium was present in the filtrate.



CdSO₄ 24H₂O sp. gr. 1.09 N. D.₁₀₀

Cd		Fe									
in grms		in grams	c.c.	Amp.	Volts	Time	Metal found	Test dep't	Test filtrate		
1. 0.2050	0.2554	1		0.8	2.75-3	1 hr. 30 min.	0.1893				
2. 0.2050	0.2554	1		0.8	3	1 hr. 30 min.	0.2182	Fe	No Cd		
			(3 c.c. NaOH)								
3. 0.2050	0.2554	1		0.8-0.9	2.5-3.5	45 min.	0.2058	Fe	Cd		
4. 0.2050	0.2554	1		0.8-0.9	3-4	45 min.	0.2070	Fe	Cd		

Therefore, no satisfactory separation of cadmium from ferric iron was obtained under these conditions. The iron tends both to hold back the cadmium, and to be partially precipitated with that metal.

2. Ferrous iron.

The attempt was next made to separate cadmium from ferrous iron. To 10 c. c. of the cadmium sulphate solution, acidulated with sulphuric acid as before, 1 gram of ferrous sulphate was added, the solution diluted to 60 c. c., and electrolyzed. In the first trial a satisfactory result was obtained. The deposit weighed 0.2053 g. (cadmium taken, 0.2050 g.), and showed no test for iron. Further, the filtrate gave no test for cadmium. Subsequent trials, however, gave low results, but the deposits were always free from iron. The higher the current, the less metal was deposited.

Attempts were made to introduce reducing agents into the electrolyte, endeavoring to keep the iron in the ferrous condition, as it was considered that the incomplete precipitation of cadmium might be due to the presence of ferric iron formed by the oxidizing action of the current. Potassium cyanide was tried, also sulphurous acid, and finally, a higher current was employed. In the last case, the cadmium was thoroughly precipitated, but the deposit was contaminated with iron.

CdSO ₄ FeSO ₄ H ₂ SO ₄ N. D. ₁₀₀							
Cd	Fe sp. gr.	1.09			Metal	Test	Test
in grams	in grams	c.c.	Amp.	Volts	Time	found	deposit filtrate
1. 0.2050	0.2+	1		3.5	45 min.	0.2053	No Fe No Cd
2. 0.2050	0.2+	1	0.8-0.85	3-3.25	45 min.	0.2012	No Fe Cd
3. 0.2050	0.2+	1	0.8-0.9	3	45 min.	0.1891	No Fe
4. 0.2050	0.2+	1	1.0	3	45 min.	0.1737	
5. 0.2050	0.2+	1	0.75-0.8	1.5-2.5	45 min.	0.1995	
1 g. KCN							
6 0.2050	0.2+	1	0.8	2.5	45 min.	0.1581	
3 drops H ₂ SO ₃							
7 0.2050	0.2+	1	0.4-0.6-1.8	1.5-3.5	45 min.	0.2065	Fe No Cd
3 drops H ₂ SO ₃							

It is evident, therefore, that with low currents, the separation of cadmium from iron is not a success. An entirely successful separation of these two metals was obtained by Miss Davison (Thesis, 1905) in twenty or twenty-five minutes, using a potassium cyanide electrolyte and a current of five amperes.

With the same current, Ashbrook found the separation possible in ten minutes, both in sulphuric acid and phosphoric acid solution.

III. Separation of cadmium from metals of Group IV.

(a.) From cobalt.

No deposit of cobalt was obtained by electrolyzing a solution containing 0.1808 g. of cobalt at 0.4 ampere and 2.5 volts for one hour and twenty-five minutes. Satisfactory separations of cadmium from cobalt were then made, as shown by the following data:

CdSO ₄ CoSO ₄ H ₂ SO ₄ N. D. ₁₀₀							
Cd	Co	sp. gr. 1.09					
in grams	in grams	c.c.	Amperes	Volts	Time	Cd found	Error in grams
1. 0.2051	0.1808	I	0.4	2.5	45 min.	0.2048	—0.0003
2. 0.2051	0.1808	I	0.4-0.5	2.5-2.75	45 min.	0.2051	0.0000
3. 0.2051	0.1808	I	0.4-0.5	2.5-3	45 min.	0.2055	+0.0004
4. 0.2051	0.1808	I	0.4-0.5	2.5-2.9	45 min.	0.2045	—0.0006

In contrast to the results under iron, the use of a low current makes possible a separation of cadmium from cobalt which is not obtained with high currents. Ashbrook tried this separation, but found that in both sulphuric acid and phosphoric acid solution, cobalt was partially precipitated. Miss Davison tried the separation of cadmium from cobalt in cyanide solution, but found that the precipitation was not complete; even after thirty-five minutes. Here, even with the low current of 0.4 ampere, the precipitation is complete in forty-five minutes. With stationary electrodes, the separation of cadmium takes place using a still lower current, 0.078 ampere, but four to four and a half hours are required.

(b.) From nickel.

It was found difficult to make a clean separation of cadmium from nickel. On first trial, no deposit was observed from 10 c. c. of nickel sulphate solution containing 0.1630 grams of nickel, electrolyzed at 0.3 ampere for forty-five minutes, using 1 c. c. of sulphuric acid, sp. gr. 1.09, as electrolyte. Separations of cadmium from nickel were then tried as follows:



CdSO ₄ Cd	NiSO ₄ Ni	H ₂ SO ₄ sp. gr. 1.09	N. D. ₁₀₀ c.c.	Amperes	Volts	Time	Cd found	Error in grams
in grams	in grams							
1. 0.2070	0.1630	1	0.3	2.5+	45 min.	0.2067	—0.0003	
2. 0.2070	0.1630	1	0.3	3.25	45 min.	0.2073	+0.0003	
3. 0.2070	0.1630	1	0.3	2.75	45 min.	0.2074	+0.0004	

These separations seemed satisfactory, but on raising the current to 0.4 ampere, deposits too high in weight were obtained.

4. 0.2070	0.1630	1	0.4	3	45 min.	0.2083	+0.0013	
5. 0.2070	0.1630	1	0.4	3	45 min.	0.2091	+0.0021	

Nickel sulphate solution was then tried alone, both at 0.4 and 0.3 ampere.

6.	0.2053	0.5	0.4	2.5	1 hr. 15 min.	0.0028		
7.	0.2053	0.5	0.3	2.3	50 min.	0.0013		

These deposits were shown to be nickel, since they gave a green solution with nitric acid. On evaporating to dryness, a black residue was obtained which dissolved in nitric acid to a green solution. The weight of these deposits corresponded closely to the error in weight of the metal in experiments 4 and 5. A series of determinations was then made, varying the strength of the current from 0.3 to 0.5 ampere, and the time of electrolysis from forty-five minutes to an hour and a half. In each case the deposit was tested for nickel with potassium sulphocarbonate and a pinkish color obtained, except in experiment 9. The filtrates seemed free from cadmium.

CdSO ₄ Cd	NiSO ₄ Ni	H ₂ SO ₄ sp. gr. 1.09	N.D. ₁₀₀ c.c.	Amperes	Volts	Time	Metal found	Test deposit	Error in grams
in grams	in grams								
8. 0.2050	0.2053	0.5	0.4	2.8	1 hr. 5 min.	0.2077	Ni	+0.0027	
9. 0.2050	0.2053	0.5	0.3	2.5	1 hr.	0.2058	No Ni	+0.0008	
10. 0.2050	0.2053	0.5	0.3	2.5	50 min.	0.2068	Trace Ni	+0.0018	
11. 0.2050	0.2053	0.5	0.3	2.5	1 hr. 5 min.	0.2060	Ni	+0.0010	
12. 0.2050	0.2053	0.5	0.3	2.5	1 hr. 5 min.	0.2071	Ni	+0.0021	
13. 0.1936	0.2053	0.5	0.4-0.5	3	1 hr. 10 min.	0.1946	Ni	+0.0010	
14. 0.1936	0.2053	0.5	0.3	2.75	1 hr. 30 min.	0.1955	Ni	+0.0019	
15. 0.1936	0.2053	0.5	0.3	2.5	1 hr.	0.1956	Ni	+0.0020	
16. 0.1936	0.2053	0.5	0.3	2.7	45 min.	0.1941	Trace Ni	+0.0005	

The best results appear to have been obtained in experiments 1-3, using 0.3 ampere for forty-five minutes. Increasing the current, or the time, seems to increase the amount of nickel in the deposit. The deposits in 1-3 were, unfortunately, not tested for nickel. The conclusions drawn from them, however, were confirmed by experiment 16, where a current of 0.3 ampere was applied for forty-five minutes. The deposit showed but a trace of nickel, and the error in weight was only 0.0005 gram.

Miss Davison, working with the cyanide electrolyte, always

found some nickel in the cadmium deposit. Ashbrook had the same experience when using phosphoric acid solution, but obtained a satisfactory separation with sulphuric acid as electrolyte, using a current of 5 amperes.

(c.) From manganese.

It was found that manganese itself is precipitated under the conditions used for cadmium. The deposit of manganese dioxide on the dish anode was not adherent, and fell in flakes upon the cathode, tending to contaminate the cadmium deposit. By reversing the poles, making the stationary dish the anode, and the rotating dish the cathode, a clean deposit of cadmium was obtained. The manganese dioxide, though not adherent, was retained upon the lower dish. There is a distinct advantage in this form of electrode, since it can be used as a cathode as well as an anode, having sufficient surface to retain firmly a deposit of 0.2 gram of metal.

A small amount of the cadmium sulphate solution, 5 c. c., (0.10255 g. cadmium), was first tried, and then the usual volume of 10 c. c. In all cases, manganese was found in the filtrates. Under these conditions, then, manganese is only partially precipitated, hence no quantitative separation of it could be made. Varying quantities of manganese were used in these experiments, but always with the result that the cadmium deposit was low in weight when as much as 0.2 g. of cadmium was employed.

CdSO ₄		MnSO ₄	H ₂ SO ₄	N. D. ₁₀₀				
Cd	Mn	Sp. gr. 1.09				Cd	Error in	
in grams	in grams	c.c.	Amperes	Volts	Time	found	grams	
1. 0.10255	0.2421	I	0.4-0.5	3-3.25	30 min.	0.1020	-0.0005	
2. 0.2051	0.0484	I	0.4-0.5	2.5-2.8	45 min.	0.2032	-0.0019	
3. 0.2051	0.0484	I	0.4-0.5	2.5	45 min.	0.2022	-0.0029	
4. 0.2051	0.0484	I	0.4-0.5	2.7-3	1 hr. 15 min.	0.2029	-0.0022	
5. 0.2051	0.0484	I	0.4-0.5-0.6	2.5-3	45 min.	0.2022	-0.0029	
6. 0.2051	0.2421	I	0.4-0.5	2.5+	45 min.	0.2031	-0.0020	
7. 0.2051	0.2421	I	0.4-0.5	2.75+	45 min.	0.2021	-0.0030	

2 drops NH₄OH

High currents are evidently best for this separation, since Ashbrook separated cadmium completely from manganese, both in sulphuric acid and phosphoric acid solution, using a current of five amperes.

The possibility of formic acid as an electrolyte for this separation was then considered, as formic acid is one of the best electrolytes for cadmium and for manganese when determined

singly. It proved to be successful. The deposits of cadmium obtained were especially beautiful, soft and velvety in appearance, and of changing shades of silver gray.

CdSO ₄		MnSO ₄	Formic	N. D. ¹⁰⁰				
Cd	Mn	Acid				Cd	Error in	
in grams	in grams	c.c.	Amperes	Volts	Time	found	grams	
1. 0.2051	0.2421	5	0.4-0.5	2.5-3	1 hr.	0.2054	+0.0003	
2. 0.2051	0.2421	5	0.4	2.5	1 hr.	0.2058	+0.0007	
3. 0.2051	0.2421	5	0.4	2.5	1 hr. 25 min.	0.2051	0.0000	
4. 0.2051	0.2421	5	0.4	2.75	45 min.	0.2045	-0.0006	

(d.) From zinc.

A satisfactory separation of cadmium from zinc was obtained. No deposit of zinc appeared from the electrolysis of 10 c. c. of zinc sulphate solution containing 0.2094 grams of zinc, using a current of 0.4 ampere for forty-five minutes. Separations of cadmium from zinc were then tried under the same conditions. The deposits were dissolved in nitric acid and tested for zinc on charcoal with the blowpipe, fusing with sodium carbonate and moistening with cobalt nitrate. No test for zinc was obtained, and the filtrates were free from cadmium.

CdSO ₄		Zn SO ₄	H ₂ SO ₄	N. D. ¹⁰⁰				
Cd	Zn	Sp. gr. 1.09				Cd	Error in	
in grams	in grams	c.c.	Amperes	Volts	Time	found	grams	
1. 0.2050	0.2094	I	0.4	2.75-2.9	45 min.	0.2053	+0.0003	
2. 0.2050	0.2094	I	0.4	3	45 min.	0.2057	+0.0007	
3. 0.2050	0.2094	I.	0.4	2.75	45 min.	0.2057	+0.0007	
4. 0.2050	0.2094	I	0.4	2.75	45 min.	0.2050	0.0000	
5. 0.2050	0.2094	I	0.4	3	45 min.	0.2048	—0.0002	

Ashbrook reports that "zinc always came down with the cadmium in sulphuric acid solution, and also in phosphoric acid solution." Here, then, is another case like the cadmium cobalt separation, in which a low current is successful where a high current has failed. Here, again, the separation may be obtained with stationary electrodes, and has been worked out with various electrolytes, but the time required is from three to ten hours.

IV. Separation of cadmium from magnesium. The experiments on these two metals also resulted in a satisfactory separation.

CdSO ₄		MgSO ₄	H ₂ SO ₄	N. D. ₁₀₀			
Cd	Mg	Sp. gr. 1.09				Cd	Error in
in grams	in grams	c.c.	Amperes	Volts	Time	found	grams
1. 0.2051	0.1785	0.5	0.4-0.5	3	45 min.	0.2055	+0.0004
2. 0.2051	0.1785	0.5	0.4-0.5-0.6	3	50 min.	0.2053	+0.0002
3. 0.2051	0.1785	0.5	0.4	2.7	1 hr. 5 min.	0.2051	0.0000

Similar results were obtained by Ashbrook with magnesium, using high currents.

B. ACETATE ELECTROLYTE.

The electrolyte used in these determinations was 1 gram of ammonium acetate together with 0.5 c. c., or more often 1 c. c., of acetic acid, 1:3 by volume (1 volume glacial acetic acid to 3 of water). The solutions were heated just below boiling before electrolyzing. This preliminary heating was found to be quite necessary, influencing the character of the deposit to a considerable extent. The deposits of cadmium from the acetate electrolyte are more coarsely crystalline than from the sulphuric acid electrolyte, and hence sometimes not adherent. If proper care is exercised, however, there need be no loss of metal. Cold water was used in washing the deposits, as in the other set of determinations.

I. Precipitation of cadmium alone.

CdSO_4 1g. $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ N. D.₁₀₀

Cd $\text{C}_2\text{H}_3\text{O}_2$ (1:3)					Cd	Error in
in grams	c.c.	Amperes	Volts	Time	found	grams
1. 0.2051	0.5	0.05	2.25	20 min.	No deposit	
2. 0.2051	0.5	0.1	2.5	25 min.	Trace of deposit	
3. 0.2051	0.5	0.15	2.7	1 hr.	0.2040	-0.0011
4. 0.2051	1	0.2	2.5	2 hrs. 30 min.	0.2054	+0.0003
5. 0.2051	1	0.2	2.5	1 hr. 5 min.	0.2041	-0.0010
6. 0.2051	1	0.05-0.3	2.3-3	1 hr.	0.2051	0.0000
7. 0.2051	1	0.3	3	1 hr.	0.2048	-0.0003
8. 0.2051	1	0.3	2.75	1 hr.	0.2052	+0.0001

0.3 ampere was, therefore, taken as the current to be used for further work. The time can be reduced to forty-five minutes.

II. Separation of cadmium from metals of Group III.

(a.) From aluminium.

It was in the course of the work on these separations that the necessity of heating the solutions before electrolysis was made evident. Several separations of cadmium from aluminium, and several determinations of cadmium alone, were tried at ordinary temperature. The weight of metal was invariably high, the deposit containing coarse crystals, and having a tendency to sponginess, and hence occluding mother liquor. On heating the solutions, however, the deposits were adherent, and not spongy, and the weights were more satisfactory. The difference in deposits from cold and hot solutions is shown as follows:

COLD

CdSO ₄ Cd	1g. NH ₄ C ₂ H ₃ O ₂ C ₂ H ₄ O ₂ (1:3)	N. D. ₁₀₀				Cd found	Error in grams
in grams	c.c.	Amperes	Volts	Time			
1. 0.1936	I	0.3	2.8	1 hr.		0.2000	+0.0064
2. 0.1936	I	0.3	3.	50 min.		0.1940	+0.0004
3. 0.1936	I	0.3	2.9	45 min.		0.1936	0.0000
4. 0.1936	I	0.3	2.8	45 min.		0.1951	+0.0015
5. 0.1936	I	0.3	3.	45 min.		0.1941	+0.0005

In experiment 3, the deposit was washed with hot water before weighing.

HOT

6. 0.1936	I	0.3	3	45 min.		0.1938	+0.0002
7. 0.1936	I	0.3	2.5	45 min.		0.1936	0.0000
CdSO ₄	Al ₂ (SO ₄) ₃	1g. NH ₄ C ₂ H ₃ O ₂					

COLD

Cd	Al					Cd	Error in
in grams	in grams	C ₂ H ₄ O ₂ (1:3)	N. D. ₁₀₀			found	grams.
		c.c.	Amperes	Volts	Time		
1. 0.1936	0.1811	I	0.3	2.7-3.2	45 min.	0.1964	+0.0028
2. 0.1936	0.2200	I	0.3	2.7	45 min.	0.1958	+0.0022

HOT

3. 0.1936	0.2200	I	0.3	2.75	45 min.	0.1934	-0.0002
4. 0.1936	0.2200	I	0.3	3	45 min.	0.1941	+0.0005
5. 0.1936	0.2200	I	0.3	2.5	45 min.	0.1946	+0.0011
6. 0.1936	0.2200	I	0.3	2.75	45 min.	0.1932	-0.0004

Experiment 5 shows that high results may be obtained even when the solution is heated before electrolysis.

(b.) From chromium.

No satisfactory separation of cadmium from chromium was obtained, but some very curious deposits attracted attention. Ammonium acetate alone, and acetic acid alone, were tried as electrolytes, as well as the combination of the two. The current was varied from 0.3 to 0.9 ampere. The chromium solution used was the green sulphate. When ammonium acetate together with acetic acid, or ammonium acetate alone, was used, the solution became yellow in color, showing oxidation. When, however, acetic acid was used alone, the color remained green. No different results were obtained from these changes in the electrolyte. The deposits were peculiar in form; the metal was deposited in ridges, radiating from a dark gray center, most of the metal being bright and silvery in appearance. There was considerable green color in the deposits, suggesting occlusion of chromium salts. Repeated washings with hot water lowered the weight of the precipitate, but did not remove the green color to any great extent. A deposit weighing 0.2274 g., after being washed with hot water, weighed successively 0.2124 g., 0.2114 g.,

and 0.2098 g. The deposit was still green in color. The cadmium taken was 0.2051 g. Cadmium was sometimes found in the filtrate, so that the weight of the deposits did not necessarily indicate complete precipitation of the cadmium. The washings were sometimes colorless, and sometimes green in color, but in both cases gave tests for a sulphate with barium chloride and hydrochloric acid. The deposits dissolved instantly in nitric acid to a green solution which, with ammonium hydroxide, gave a gray-green precipitate, showing the presence of chromium in some form.

(c.) From iron.

1. Ferric iron.

As in the case of chromium, no satisfactory results were obtained. The same variation in the electrolyte was employed as under chromium, ammonium acetate alone, acetic acid alone, and the combination of the two. The current was varied from 0.3 to 0.9 ampere. The deposits were spongy and dark, with traces of basic salt. They had the appearance of containing iron, and always gave evidence of that metal by the sulphocyanate test.

2. Ferrous iron.

One gram of ferrous sulphate was used, and the customary amount of ammonium acetate and acetic acid. In two experiments, using 0.3 ampere for forty-five minutes, the following results were obtained:

Cd present	Cd found	Error in grams
0.1936	0.1980	+0.0044
0.1936	0.1819	-0.0117

One deposit was high, the other low in weight, but both had the appearance of containing iron, and both gave tests for that metal.

III. Separation of cadmium from metals of Group IV.

(a.) From cobalt.

When a solution of cobalt sulphate (0.1808 g. cobalt) was subjected to electrolysis at 0.3 ampere with the acetate electrolyte (1 g. ammonium acetate and 1 c. c. acetic acid 1:3), the solution turned brown, indicating oxidation, and there was a slight metallic deposit on the cathode and also on the anode. These deposits dissolved in nitric acid, the heavier cathode deposit giving a pink solution, the anode deposit a colorless solu-

tion. Sodium hydroxide, however, gave a dark precipitate with this colorless solution, and on testing this precipitate with a borax bead, a blue color was obtained. Hence both deposits were evidently cobalt.

CoSO ₄ 1g. NH ₄ C ₂ H ₃ O ₂ N.D. ₁₀₀					
Co	C ₂ H ₄ O ₂ (1:3)				Co
in grams	c.c.	Amperes	Volts	Time	found
1. 0.1808	1	0.3	2-2.25	1 hr	0.0176
2. 0.1808	1	0.3	2.5-3	1 hr.	0.0339

Therefore, no separation of cadmium from cobalt could be expected under these conditions.

(b.) From nickel.

Similar results were obtained with nickel.

NiSO ₄ 1g. NH ₄ C ₂ H ₃ O ₂ N.D. ₁₀₀					
Ni	C ₂ H ₄ O ₂ (1:3)				Ni
in grams	c.c.	Amperes	Volts	Time	found
0.2053	1	0.3	2+	1 hr.	0.0392

Treatment of the deposit with nitric acid gave a green solution which turned blue when made ammoniacal.

(c.) From manganese.

The rotating dish cathode was again employed, but the weight of the metal was always low. The deposits were adherent, and finely crystallized, but had none of the velvet-like appearance given by the formic acid electrolyte.

CdSO ₄ MnSO ₄ 1g. NH ₄ C ₂ H ₃ O ₂ N. D. ₁₀₀					
Cd	* Mn	C ₂ H ₄ O ₂ (1:3)			Cd
in grams	in grams	c.c.	Amperes	Volts	Time
1. 0.1936	0.2421	1	0.3	1.5-2.5	45 min.
2. 0.1936	0.2421	1	0.3	1.5-2.5-3.2	45 min.
3. 0.1936	0.2421	1	0.3	1.5-3	1 hr.
					found
					0.1907
					0.1893
					0.1869
					Error in
					grams
					—0.0029
					—0.0043
					—0.0067

(d.) From zinc.

As in the case of cobalt and nickel, zinc begins to be deposited at such low currents with an acetate electrolyte that no separation of cadmium from zinc is possible at 0.3 ampere.

ZnSO ₄ NaC ₂ H ₃ O ₂ N. D. ₁₀₀					
Zn	C ₂ H ₄ O ₂ (1:3)				Zn found
in grams		Amperes	Volts	Time	
1. 0.2094		0.2	3	30 min.	0.0496
2. 0.2094		0.2	3-2.5	1 hr.	0.0529

IV. Separation of cadmium from magnesium. This separation was successful.

	CdSO ₄ Cd	MgSO ₄ Mg	1g. NH ₄ C ₂ H ₃ O ₂ C ₂ H ₄ O ₂ (1:3)	N. D. ₁₀₀			Cd	Error in
	in grams	in grams	c.c.	Amperes	Volts	Time	found	grams
1.	0.2051	0.1785	1	0.3	2.8	1 hr.	0.2049	—0.0002
2.	0.2051	0.1785	1	0.3	2.7	1 hr.	0.2054	+0.0003
3.	0.2051	0.1785	1	0.3	2.5-3	50 min.	0.2050	—0.0001
4.	0.2051	0.1785	1	0.3	2.5	55 min.	0.2048	—0.0003
5.	0.2051	0.1785	1	0.3	2.5-3.3	45 min.	0.2050	—0.0001

The method of testing the filtrates in this work should be mentioned. The filtrates were evaporated to a small bulk, and tested for cadmium with hydrogen sulphide. In the sulphuric acid solutions, slight yellowish-brown precipitates, suggesting cadmium sulphide, were obtained in varying amounts. With the acetate solutions, no yellow precipitates were obtained. A clear yellowish color was sometimes observed in the solution when the hydrogen sulphide was first added, and a grayish precipitate of sulphur separated out on further treatment with the gas. In general, the solution was perfectly colorless, and gave no evidence of cadmium. Cadmium deposits from the same amount of cadmium sulphate solution (10 c. c.) weighed no more from the acetate electrolyte than from the sulphuric acid electrolyte. Hence it was concluded that if the yellowish-brown precipitates obtained were cadmium sulphide, only a trace of cadmium was represented by them.

The question arose as to how much the particular form of anode used in this work influenced the time necessary for a determination. The dish anode should reduce the time factor greatly, judging by its action in previous work. To answer this question more definitely, the spiral anode was substituted in a determination of cadmium from 10 c. c. of cadmium sulphate solution, containing 0.1936 g. cadmium. One c. c. sulphuric acid (1.09) was used as the electrolyte, and 0.4 ampere as the current. After forty-five minutes, the current was interrupted. The deposit of cadmium obtained weighed only 0.1742 g., proving that complete precipitation of the metal by use of the spiral anode would require more time than by use of the dish anode.

CONCLUSION.

The object of this investigation, as stated in the introduction, was *first*, to prove whether satisfactory separations of metals could be made with the rotating anode using low currents, and *second*, to throw some light on the question whether the rapid methods of electrolysis are of practical value in conducting separations.

The first question is certainly answered in the affirmative.

Separations of cadmium were made from aluminium, chromium, cobalt, nickel, zinc, and magnesium, with the sulphuric acid electrolyte, from manganese with formic acid as electrolyte, and from aluminium and magnesium with the acetate electrolyte.

As to the practical value of the work, a comparison should be made of these results with the results obtained with stationary electrodes, and with the rotating anode, using high currents. This comparison is best made in tabular form.

TABLE I.

Sulphuric Acid Electrolyte
Separations of Cd from

	Stationary Electrodes		Rotating Anode Low Currents		Rotating Anode High Currents	
	Amperes	Time	Amperes	Time	Amperes	Time
Al	.078	4-4½ hrs.	0.4	45 min.	5	10 min.
Cr	.078	4-4½ hrs.	0.4	1 hr.	Not successful	
Fe	.078	4 4½ hrs.	Not successful		5	10 min.
Co	.078	4-4½ hrs.	0.4	45 min.	Not successful	
Ni	.078	4-4½ hrs.	0.3	45 min.	5	10 min.
Mn	.078	4-4½ hrs.	Not successful		5	10 min.
Zn	Not recorded		0.4	45 min.	Not successful	
Mg	Not recorded		0.4	45 min.	5	10 min.

TABLE II.

Separations of Cd from

Phosphoric Acid Electrolyte			Acetate Electrolyte	
High Currents			Low Currents	
	Amperes	Time	Amperes	Time
Al	5	10 min.	0.3	45 min.
Cr	5	10 min.	Not successful	
Fe	5	10 min.	Not successful	
Co	Not successful		Not successful	
Ni	Not successful		Not successful	
Mn	5	10 min.	Not successful	
Zn	Not successful		Not successful	
Mg	5	10 min.	0.3	45 min.
Formic Acid Electrolyte				
Low Currents				
	Amperes	Time		
Mn	0.4	1 hr.		



Table I shows, at once, the advantage of rotation, even with low currents, over stationary electrodes. A comparison of Tables I and II brings out the following points in regard to rotation with high and with low currents:

1. Separations of cadmium from aluminium and magnesium are possible in all cases studied.
2. The best conditions for the separation of cadmium from chromium are with a high current and phosphoric acid as electrolyte, although the separation is possible with a low current in sulphuric acid solution.
3. The separation of cadmium from iron is possible with a high current, but not with a low current.
4. Separations of cadmium from cobalt and zinc are possible with a low current, but not with a high current.
5. The separation of cadmium from nickel is possible with both a high and a low current, but a high current is to be preferred.
6. The separation of cadmium from manganese is best made at a high current, but may be made at a low current, if formic acid is the electrolyte.

This study is, of course, only a fragment of what must be done to make clear the possibilities of electrolytic separations. Work with cadmium should be extended, using other metals and other electrolytes. Each metal in turn should receive such a complete treatment. High current separations need further study as well as low current separations, as the work already done has been confined to comparatively few metals.

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